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FINAL REPORT

PROPERTIES OF NON - STOICHIOMETRIC

METALLIC CARBIDES

ADVANCED METALS RESEARCH CORPORATION

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FINAL REPORT

PROPERTIES OF NON-STOICHIOMETRIC METALLIC CARBIDES

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Properties of Non-Stoichiometric Metallic Carbides

ABSTRACT

In a project whose ultimate aim is the examination of the properties of non-stoichiometric metallic carbides, the present work is concerned with carbides of the Group IV metals. The lattice parameter-composition relationship for the cubic TiC phase has been determined which shows a maximum value at $TiC_{0.85}$ of 4.3305A. The maximum carbon content of this phase corresponds to $TiC_{0.95}$. The production of dense high purity bodies of titanium and zirconium carbide bodies of a range of carbon contents has been examined by sintering and zone melting techniques. Dense polycrystalline bodies can be produced by an activated sintering technique but induction zone melting is required for large monocrystalline specimens.

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Properties of Non-Stoichiometric Metallic Carbides

I. Introduction

For many years the carbides of the transition metals found in Groups IV, V and VI of the periodic table of the elements have been subjects of considerable interest. The combination of metallic behavior with high hardness and high melting point suggests a unique nature of the structure; but, in spite of the very considerable study to which these substances have been subjected over the years, the picture of their basic constitution and the relationship between structure and properties is still far from clear.

One road leading to a satisfactory understanding of the basic constitution of these substances and to an appreciation of possible useful applications is an experimental one involving the careful determination of the fundamental physical properties. A significant feature is that many of these carbides exist as single phases over a considerable range of composition and consequently, the non-stoichiometric compositions become of particular importance.

Probably the principal reason for present lack of understanding of the carbides and the other related interstitial compounds has been the experimental difficulty of preparing suitable samples for examination, samples of high purity and

of complete homogeneity and density. The high temperatures
involved and the rather high reactivity of the constituents
at these temperatures have posed a problem which has not as
yet been completely solved. It should be pointed out that
for the measurement of some of the properties of interest,
powders of high purity will serve as specimens. For other
property measurements a poly-crystalline specimen, provided
it is of one phase and completely dense,will serve. The
most suitable specimen for most measurements and a positive
requirement for some is a single crystal having a high de-
gree of perfection. The problem of specimen preparation
far outweighs the problems of measurement and probably even
the problems of interpretation.

The present investigation is limited to carbides of
metals of Group IV, i.e., titanium, zirconium and hafnium.
The first step has been to make a critical survey of the
available information on the phase diagrams of these three
systems and to fill in experimentally the missing informa-
tion on the crystal structures. Since each of these systems
forms only a single carbide phase with a cubic structure of
B-1 type, the crystal structure data needed is principally
that of the variation of lattice constant with carbon con-
tent. The second step has been to investigate several pro-
cedures for obtaining dense specimens of the required high
purity and their conversion into single crystal form.

These two steps form the subject of the present report. The experimental work reported has been primarily on the titanium-carbon system with a minor amount on the zirconium and hafnium systems. Because of the similarities, successful procedures established for titanium carbide should be directly applicable to the others.

II. Phase Diagrams of the Ti-C, Zr-C and Hf-C Systems

A critical review of the published work on the carbides of Groups IV, V and VI has been presented by Storms[1] in which the phase diagrams of the Group IV carbides are discussed. This represents the situation up to 1962.

A. Phase Diagram of Ti-C System

Fig. 1 shows the diagram essentially as given by Storms[1] on the basis of what he considers the most reliable results. Its most important features in so far as the present work is concerned are the Ti-TiC eutectic temperature of 1645°C, the TiC-C eutectic at 2610°C, the maximum melting temperature of TiC at 3180°C and the range of the TiC phase extending from $TiC_{0.49}$(32.9 at % carbon) to $TiC_{0.98}$(49.5 at % carbon). The composition of congruent melting is placed at about $TiC_{0.88}$(46.8 at % carbon).

B. Phase Diagram of Zr-C System

Fig. 2 shows the phase diagram of the Zr-C system based primarily upon the work of Dolloff[2]. The results of

Farr[3] and of Benesovsky and Rudy[4] are also of interest. The
significant features of the diagram are the Zr-ZrC eutectic
temperature at 1850°C, the ZrC-C eutectic at 2860°C and the
maximum melting point at 3420°C, corresponding to a composi-
tion of $ZrC_{0.82}$(45 at % carbon). The range of the ZrC phase
is from $ZrC_{0.63}$(38.5 at % carbon) $ZrC_{.95}$(48.9 at % carbon).
In this system it appears quite definite that the maximum
carbon content of the mono-carbide phase is less than $ZrC_{1.0}$
and that the congruent melting point is at a composition
lower than the maximum carbon content, a situation that applies
to Ti-C and probably to Hf-C. It should be noted that the
solidus line representing the low carbon boundary of the ZrC
field is essentially vertical at the lower temperatures, in
contrast to the Ti-C system.

C. Phase diagram of Hf-C System

A phase diagram of the Hf-C system has been presented
by Benesovsky and Rudy[4] and its essential features are shown
in Fig. 3. The Hf-HfC eutectic temperature is 2000°C, the
Hf-C eutectic temperature is 3000°C and the congruent melt-
ing temperature is estimated at 3900°C at $HfC_{1.0}$. Krikorian[5]
has reported slightly lower values for the eutectic tempera-
tures. The Russian workers Avarbe et al[6] have presented a
somewhat different diagram in which liquid and carbide react
by a peritectic reaction at 2820°C to form α Hf. In both dia-
grams, the range of the carbide phase is indicated as from
about $HfC_{0.55}$(35.4 at % carbon) to $HfC_{1.0}$(50 at % carbon).

III. Structure of the Monocarbide Phases

A. General

The transition metals of Group IV each form a single monocarbide which has the B-1 structure type, that is, a face centered cubic lattice of metal atoms with the carbon atoms in the octahedral interstices. Since it is observed that the cubic phase is stable over a considerable range of carbon contents less that the stoichiometric composition, it appears that a significant number of the octahedral sites may be vacant without destroying the stability of the face centered cubic lattice, a lattice type not exhibited by the pure metals.

If one considers the carbide phases on the basis of a hard sphere model, it is possible to calculate the lattice constant, using the radii of the metal ions from the pure metals and the covalent radius of carbon. It is interesting to compare the results of such calculation for the three stoichiometric carbides involved as shown in Table I.

Table I
Comparision of Calculated & Observed Lattice Constants

Carbide	A_o Calculation	A_o Observed
TiC	4.44 A	4.33 A
ZrC	4.70 A	4.70 A
HfC	4.68 A	6.64 A

It is clear that while ZrC and HfC are in reasonable agreement with the predicted values, the parameter of TiC is significantly smaller than predicted. This observation may prove to be significant in relation to the homogeneity range and the properties of the TiC phase.

B. Lattice Parameter-Composition Relationships

The variation of the lattice parameter with carbon content over the homogeneous range of the cubic phases in the three systems is of particular interest. Establishment of this relationship is important in the high purity alloys from the point of view of establishing the composition range of the phase, as a means of determining the composition of the carbide phase in two phase alloys and of course, for any fundamental consideration of the true nature of these substances.

In the case of the TiC system, data is available from two sources, Ehrlich[7] and Cadoff et al[8]. The results are shown in Fig. 4. Ehrlich's data has been corrected to angstrom units instead of KX units to place it on a comparable basis, but even so there are important discrepancies. It has been suggested that Ehrlich's results are low because of contaminations of his specimens. Cadoff and Nielson had too few compositions to establish the relationship with the desired accuracy. It is obvious that additional work is

required in this area and the experimental results in this direction are reported in Section IV.

The variation of lattice parameter with carbon content in the ZrC system has been reported by Benesovsky and Rudy[4] in 1960 and by Dolloff[2] in 1962. These results are shown in Fig. 5. It is clear that there is considerable disagreement. The Austrian workers started with hydride and carbon and used a hot pressing technique at 1400°C in an argon atmosphere. Dolloff used the same starting materials but most of his results were obtained by sintering in vacuum at temperature above 3000°C. The two investigations agree fairly well on the lower limit of the composition of the ZrC phase but Dolloff's parameter values are significantly higher. An important feature of Dolloff's result is the fact that the upper limit of the phase is $ZrC_{0.96}$ (48.9 at % carbon) which is definitely short of the stoichiometric composition and that the parameter curves goes through a broad maximum at about $ZrC_{0.80}$ (44.4 at % carbon) where the lattice parameter reaches a value of 4.702A. Again, because of the differences in reported results, an experimental program was undertaken which is reported in Section V.

Benesovsky and Rudy[4] reported a lattice parameter composition curve for the HfC system. It shows the lattice parameter increasing from 4.614A to 4.628A over the range of $HfC_{0.6}$ (37 at % carbon) to $HfC_{1.0}$ (50 at % carbon). An

experimental investigation of this system has been initated but no results can be reported at this time.

IV. Lattice Parameter Measurements in the TiC Systems

A. Experimental Procedures

The starting materials for the Ti-C systems were titanium hydride (Metal Hydrides Grade E) and spectroscopic grade graphite. The materials were throughly mixed and heated in crucibles of high purity graphite which had been pre-fired in vacuum. Specimens of carbon content less than $TiC_{0.6}$ were compacted with 1% of paraffin in order to obtain a better reaction at the lower temperatures. Specimens of higher carbon content were placed in the graphite crucibles as loose powder.

Heating was done in a high temperature vacuum furnace with a tantalum resistance element (Brew, Model 400B). The specimens were carried through the hydrogen evolution range (about 600°C) and the Ti-C reaction range (about 1400°C) very slowly to prevent loss of specimen and overheating through the latter due to the exothermic reaction. Temperature measurement was by optical pyrometer using the known pre-cautions. After the completion of the hydrogen evolution phase and the Ti-C reaction the pressure in the furnace dropped rapidly to about 4×10^{-5} mm and was maintained below this level throughout the remainder of the run. Upon turning

off the power, the specimen cooled from 1900°C to about 1000°C in about 4 minutes.

Upon removal from the furnace, the specimens were broken up. Portions were mounted for metallographic examination, other portions ground in a mullite mortar for x-ray examination and the remainder was available for chemical analysis. The carbon analysis was carried out by the standard method for total carbon and free carbon, the combined carbon being obtained by difference. The oxygen analysis technique was the conventional method of vacuum fusion. The combined carbon analysis is reproducible to $\pm$ .01 in the value of the mole fraction while the oxygen analysis is reproducible to $\pm$ 50 parts per million.

The x-ray analysis was carried out on a Norelco diffractometer using high purity silicon as a reference material. For those compositions where the lines did not overlap, the silicon powder was used as an internal standard. The reproducibility of the lattice parameter under normal conditions is $\pm$ 0.0002A while with specimens having sharp and highly resolved lines and with the internal silicon standard, values of $\pm$ .0001A were obtained repeatedly. The absolute value is related to a lattice constant for silicon of 5.43062 A.U. Copper K alpha radiation was used throughout.

Metallographic polishing of the very brittle and often quite porous specimens presented a special difficulty. It was soon discovered that the early stages of polishing produced a severe shattering of the structure which was not removed by the later stages and gave a completely erronious image of the microstructure. After investigating several techniques, a procedure was developed to give satisfactory results which involved rough grinding on abrasive papers thru 600 grit using paraffin dissolved in kerosene as a lubricant. This was followed by 5 micron diamond grinding on a broadcloth wheel and the final polishing was done on a lead lap using one micron alumina abrasive. All stages of the polishing must be handled carefully to prevent chipping the carbide which is hard but at the same time quite fragile. The presence of excess metal phase or graphite is readily observed without etching but the carbide grain boundaries are revealed by etching with a mixture of 10 parts conc. HF, 5 parts conc. HNO_3, 40 parts glycerine.

B. Lattice Parameter Results

The specimens used for the lattice parameter-composition curve for the Ti-C system are described in Table II and are plotted in Fig. 6. It is important to note that all compositions are plotted as combined carbon in the carbide phase even though some of the high carbon specimens were actually two phase samples with some free graphite.

The important features of the curve are the upper limit of the carbon content, the maximum in the lattice constant and the low carbon limit. At 1950°C the maximum value of the combined carbon corresponds to a mole ratio of $TiC_{0.95}$. This is definitely short of the stoichiometric composition and appears to be a real characteristic of the system. It is in agreement with the common experience of the difficulty of obtaining a completely carburized specimen. Specimen T24-5 which is the terminal point of the curve contains 0.027 wt.% oxygen. A simple calculation shows that this corresponds to 1 oxygen atom to about every 50 unoccupied octahedral sites in the $TiC_{0.95}$ composition. Under these circumstances one cannot believe that the prescence of this much oxygen can be the limiting factor in the carbon content particularly in view of the fact that excess carbon is available in the specimen. The same situation was observed by Dolloff[2] for the Zr-C system.

The maximum in the lattice parameter curve appears at approximately $TiC_{0.85}$ and again reflects the same behavior as the Zr-C system. It is difficult to understand how the addition of carbon atoms to vacant interstitial sites could cause the lattice constant to increase and then decrease. An interesting speculation has been presented by Rostocker[9] in the case of TiO which is isomorphous with TiC and where the lattice constant decreases with increasing oxygen content. This is based on the idea that the stability of the cubic

phase is determined by a specific number of valence electrons per unit cell and that as the oxygen content increases a few of the titanium atom sites must be vacated in order to prevent this number from exceeding the critical value. The lattice parameter decreases as a result. It is difficult to see just how this could apply to TiC but the existence of vacant Ti sites could be checked by comparing precisely measured densities with those calculated from the x-ray data.

The low carbon end of the parameter-composition curve has presented some serious problems. On the basis of microscopic examination, the lower limit of the phase should be placed at $TiC_{0.53}$, with a lattice constant of 4.300A. However, a significant number of specimens, which are clearly of two phases, give values of the lattice parameter considerably lower than this value. Some show rather broad diffraction lines but others are quite sharp with a well resolved K alpha doublet so that the cubic phase parameter cannot be in doubt. Until this dilemma has been resolved by further experimental work, there will continue to be an element of doubt as to the low carbon limit of the cubic carbide phase.

The problem of oxygen contamination has been much discussed and it has been generally accepted that a significant content of oxygen causes low values of the lattice constant. It is interesting to examine the oxygen contents of the specimens of Table II. It will be observed that the oxygen content

increases with decreasing carbon content at the high tem-
perature, i.e. 1950°C and increases with decreasing treat-
ment temperature. Since all sintered specimens were treated
under identical conditions in so far as atmosphere was con-
cerned, one may assume that the oxygen was contained in the
starting powders and was removed to a greater or less extent
during the heat treatment. It appears, therefore, that
reasonably low oxygen contents can be achieved only by sin-
tering at high temperatures. The specimen T24-20 marked with
a square in Fig. 6 which was melted has relatively lower oxy-
gen and again emphasizes the value of the high temperature
in reducing the oxygen content.

Judging from the fit of the experimental points to a
smooth curve, it seems quite clear that an oxygen content
varying from 0.01 to 0.10 wt% produces very little shift in
the lattice parameter, at least on the scale at which Fig. 6
is plotted.

Aside from the oxygen contamination, a high degree of
purity has been maintained in the sintered samples. Speci-
men T24-23 was selected as typical and a spectroscopic analy-
sis made. The result is reported in Table III. It will be
observed that the purity is as good or better than the start-
ing titanium hydride except for copper which is tracable to
the screening operation used in preparing the specimen for
analysis.

V. Lattice Parameter Measurements in Zr-C System

Although the results of Dolloff[2] on the parameter-composition curve for Zr-C seem quite complete, the differences with the results of Benesovsky & Rudy[4] made an experimental confirmation desirable. Starting with high purity zirconium hydride (Metal Hydrides, Grade R) and following the same procedure described in Section 4, a series of specimens was prepared covering the homogeneity range. Measurements on these specimen are reported in Tabel IV.

Comparing these with the results shown in Fig. 5, it is seen that the melted samples which were heated above 3420°C in argon agree quite well with Dolloff and with Farr[3]. On the other hand, specimens of lower carbon content which were prepared at much lower temperature fall far below Dolloff's curve and are more nearly in line with the results of Benesovsky and Rudy whose specimens were prepared by hot pressing at 1400°C.

Since the specimens examined gave x-ray diffraction patterns with sharp lines and well resolved K alpha doublets, there can be little question that the metal carbon reaction in the range of 1800 to 2200°C has gone to completion and that the diffraction patterns represent homogeneous phases. However, the phases are not binary Zr-C phases but rather a solid solution, probably Zr(C,O). Only by going to very

high temperatures is the oxygen, which seems inherent in this method of preparation, reduced to acceptable levels. Clearly 2200°C is not enough in this system. Knowledge of the oxygen content of these specimens would, of course, clarify the picture but unfortunately it was impossible to obtain the complete analytical data prior to the termination date of the present contract.

Thus there appears little reason to doubt the reliability of the Dolloff curve over most of the carbon range. There is still some question about the low carbon limit of the range and the elimination of oxygen at low carbon contents. The results emphasize the desirability of a melting procedure for the production of high purity binary alloys.

VI. Production of Dense Bodies

A. Sintering Methods

Because of the high melting temperature of the carbides, the direct sintering at any reasonable temperature in vacuum does not appear feasible. It is necessary to take advantage of the temporary presence of a liquid phase to promote densification. Two methods were studied, both carried out in high vacuum. The first of these has been called " self-sintering" and is applicable to the low carbon end of the carbide range. The second is the "fugitive" binder technique which might also be referred to as activated sintering.

The self-sintering method is based upon the slope of the solidus curve which forms the low carbon boundary of the carbide phase. For instance, referring to Fig. 1 a specimen of $TiC_{0.5}$ heated to 1800°C and held in this two phase field of liquid plus solid should come to equilibrum with a small amount of liquid titanium present and should rapidly sinter into a dense body with liquid phase at the grain boundaries. If now the temperature is dropped to just below the eutectic temperature of 1650°C, the liquid phase should react with the carbide and disappear, leaving a dense single phase specimen.

Unfortunately, the desired result is not realized in practice. The specimens show ample evidence of sintering and grain growth but they contain many large pores and there are often definite traces of liquid phase remaining at grain boundaries. Fig. 7 is typical of the structures observed. The explanation of the porous structure seem to be that on heating slowly to prevent the violent exothermic reaction of titanium and carbon, a very considerable amount of carbide is formed below the eutectic temperature in the form of a rather loose skeleton throughout the sample, perhaps reflecting the sizes of the original hydride particles. The resulting pores are too large to be swept out by the moving grain boundaries and are often trapped within the grains. Even very long sintering times would be unlikely to remove them.

Obviously a possible method to overcome the porosity would be to regrind the specimens to a very fine particle size after the first sintering and resinter, then repeat the operation perhaps several times. Unfortunately, no method comminution has been discovered which does not involve a prohibitive amount of contamination and a chemical treatment such as acid leaching does not seem desirable for a very fine powder. Because of this and the fact that the method is limited to the low carbon range, further study of this technique has been discontinued.

The fugitive binder technique has been used successfully to produce dense bodies of refractory substances at reasonable sintering temperature. In this method a low melting metal, usually of the iron group, is added to the carbide in amounts ranging from 0.5 to 5% in intimate mixture. After sintering at normal temperatures and attaining full density the temperature is raised to a high value in a high vacuum environment so that the auxillary metal is evaporated out as completely as possible.

This method has been investigated for the Ti-C system for specimens covering the homogeneity range. After a preliminary sintering, the specimens were crushed and then ground for 24 hours in a small stainless steel ball mill, using benzine and about 1 percent of paraffin. a considerable pick up of iron resulted. The mill was thoroughly

flushed with argon and sealed before grinding. After grinding, the powder was compacted, placed in graphite crucibles and sintered in high vacuum at 1950°C for 3 hours. Fig. 8A is typical of the structure observed. The compact was dense with polyhedral carbide grains outlined by the iron-rich liquid phase, a typical cemented carbide structure. In the unetched condition the iron-rich areas are seen and after etching the carbide grain boundaries are revealed.

An electron microbeam analysis of the structure showed the iron to be confined to the grain boundary material and no iron was observed in the grains themselves. Fig. 8B is a microbeam scanning display of the same specimen, showing the iron rich areas. (Note the increased magnification in this figure.)

Obviously 1950°C is not high enough to evaporate the iron so specimens were reheated at 2200°C for 3 hours. A typical result is shown in Fig. 9. Fig. 9A is a $TiC_{0.85}$ specimen with added iron sintered at 1950°C for 2 hours. Fig. 9B is the same composition treated at 1950°C followed by 4 hours at 2200°C. Under these conditions most of the iron-rich phase has disappeared and a specimen of high density and large polyhedral grains results. Traces of the second phase are still observable in the etched specimen at triple points where three grains come together but slightly higher temperatures and somewhat longer times

would completely remove the unwanted phase. For the higher carbon contents where the evaporating temperature is within the single phase field of the carbide, this technique offers good promise for the production of dense polycrystal specimens suitable for the measurement of those properties for which a polycrystalline material is suitable.

B. Zone Melting Methods

Zone melting procedures appear to hold the greatest promise of producing high purity dense crystals of reasonable size. Two possibilities exist, one employing electron beam heating which requires a high vacuum and the other high frequency induction heating which may be carried out in an atmosphere of an inert gas to retard the evaporation rate of the molten carbide.

Electron beam melting experiments were carried out on Ti-C specimens in a small laboratory unit of conventional design capable of melting rods of about one quarter of an inch diameter. The starting material was in the form of short sintered rods made from hydride-carbon mixtures with a density of about 85%. The rods were supported between carbon rods in the electron beam apparatus and further sintered by passing the heated zone up and down. Above about 2600°C the situation became unstable and localized arcing took place between the specimen and the shield of the electron source. This arcing was concentrated on specific points

of the specimen causing local heating and excessive evaporation of titanium so that the operation was interrupted. It was not possible to obtain a molten zone across the diameter of the specimen. Metallographic examination showed that the center of the cross section was quite porous but the surface spots, where arcing and local melting took place, were dense and polycrystalline.

All of the experience with electron beam melting indicated that the evaporation rate in high vacuum is too rapid at the melting point to maintain the stable conditions which are required for zone melting and further work along this line was discontinued.

The above experience indicated that an inert atmosphere is required and this in turn indicates a high frequency induction heating source. An apparatus of this type was in operation at the Arthur D. Little Inc. Laboratories in Cambridge, Mass. and arrangements were made to run two specimens of TiC to test the feasibility of this method of zone melting. The writers wish to express their grateful acknowledgement to this organization and in particular Dr. G. Feich, Gerald Clay and Wilson Menashi for their willing cooperation and assistance in this regard.

The starting rods used in the induction melting were made from titanium hydride and carbon from the same source as used in the sintering experiments. The mixtures were

adjusted to give nominal carbide compositions having mole
ratios of .70 and 1.2, about 1% of paraffin was added and
the powders packed tightly into a graphite tube of three
eighths of an inch inside diameter. Special pains were
taken to make the packing as uniform as possible. The tube
with the powder was then sintered at 1100°C for one hour in
a hydrogen atmosphere.

As a result of this treatment, the specimens densified
sufficiently so that they could easily be removed from the
graphite tube and they were then transferred to the high
vacuum furnace and sintered for 1 hour at 1800°C. The re-
sulting rods were about five sixteenths of an inch in dia-
meter and four inches long, strong enough for handling and
with a density of about 85% of the theoretical carbide den-
sity.

The induction melting apparatus is described in detail
in a technical report ASD-TRD-62-204 Part I[10]. Briefly, it
consists of a pair of water cooled clamps which support the
rod in a vertical position and an induction coil which
surround the rod of such dimensions that it heats a narrow
zone. The coil is movable up and down over the length of
the rod. The whole is enclosed in a glass bell jar which
can be evacuated and filled with inert gas. In these runs,
the bell jar was filled with purified argon. A static en-
vironment of about one atmosphere pressure was maintained
during the run.

The melting of the high carbon specimen went very smoothly and a fairly uniform molten zone traversed about three inches of the specimen length. Upon removal, the rod was a bright metallic gray color. On the other hand, the nominal 0.7 mole ratio specimen gave much more trouble and appeared to be unstable. It was difficult to maintain a uniform molten zone and the specimen when completed showed a number of molten regions separated by unmelted sections. In addition, the surface of the specimen was discolored and dull as compared with the high carbon specimen which was clean and bright. It is not clear on the basis of a single run whether the difficulty with this specimen is inherent in the composition or is the result of the condition of the starting rod. It is suspected to be the latter.

The two specimens were cut up and samples taken for chemical and x-ray analysis and metallographic examination. The specimens are designated at T24-4 and T24-20 and the results of the analysis are given in Table II. They are also included in the plot of Fig. 6. In the case of T24-20, only those portions of the rod which were clearly molten were included in the analysis. It is interesting to see that in T24-20 which was analyzed for oxygen, the value is low and that the lattice parameters of both samples fall closely on the curve of the sintered specimens.

The microstructure of specimen No. T24-20 is shown
in Fig. 10 and is taken from the center of one of the molten
sections. Within this region the structure is dense with
only a few very small pores widely separated. The grain size
is fairly large and in the etched condition the grain bound-
aries are sharp and free of any traces of second phase. If
this structure could be maintained over a considerable length
of rod, very satisfactory specimens would result.

The microstructure from two areas of specimen No. T24-4
are shown in Fig. 11. Believing that carbon would be lost
during melting, the starting composition was set a little too
high in carbon and most areas of the final rod show the pre-
sence of the TiC-C eutectic at grain boundaries. Fig. 11A is
an area with a particularly large amount of eutectic while
Fig. 11B is another area where within the field of view one
sees regions with and without eutectic. The clear regions
when etched show grain boundaries under the microscope but
the boundaries are so tight and contrast between grains so
low that they do not appear in reproduction.

The variations in microstructure within a given speci-
men indicate the need for better control of the melting
process and it appears that one important area of control is
the structure of the starting rod. If the starting rod is
porous as in the present instance, liquid from the molten

zone infiltrates the region immediately adjacent, to a greater or less degree depending on the porosity, and this undoubtedly contributes to the lack of uniformity. Only by a very rigid control of the many parameters involved in the process can the method produce specimens consisting of large uniform crystals.

The Arthur D. Little, Inc. Laboratories has previously made zone melting runs on zirconium carbide and kindly supplied small portions of three such specimens together with the carbon analysis. These samples, designated as Z4-1, Z4-2 and Z4-3 were mounted, polished for microscopic examination and their lattice parameters measured. The latter results are included in Table III and plotted in Fig. 5. It will be seen that the lattice parameter values are in quite good agreement with the results of Dolloff[2].

Under the microscope specimens Z4-2 and Z4-3 appeared single phase and completely dense. Specimen Z4-1 which had an excess of carbon showed areas of the ZrC-C eutectic at grain boundaries. From the small samples available for examination little can be said about the macroscopic grain size in these materials.

VII. Conclusions

1. The lattice parameter-composition curve for the TiC system has been established at least in the range from $TiC_{0.7}$

to the upper limit, $TiC_{0.95}$. The low carbon portion of the curve is still somewhat uncertain because of the relatively high oxygen content of the specimens.

2. The lattice parameter-composition results for the ZrC system, except for molten specimens, do not confirm the results of Dolloff, probably because of serious contamination with oxygen.

3. It is essential to use very high sintering temperatures or to melt the specimens in order to reduce oxygen content to acceptable values.

4. A sintering technique employing a metal such as iron as a fugitive binder which is removed by evaporation appears to be a suitable method for preparing dense polycrystalline bodies. The final sintering must be done at temperatures above 2200°C in a high vacuum.

5. Direct zone melting using electron beam heating in a high vacuum does not appear feasible.

6. Zone melting by high frequency induction heating in an inert atmosphere appears quite feasible and is the most promising method for the production of high purity single crystal specimens suitable for basic property measurements. The method requires considerable development to the point where consistent and reproducible results can be obtained but unquestionably the potential is there and the development should be pursued vigorously.

ACKNOWLEDGEMENTS

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TABLE II

Ti-C Specimens for Lattice Parameter Measurement

Spec. No.	Ratio	Temp	Time	T.C.	C.C.	Wt.%0	a_o
T24-5	.954	1950	2	19.46	19.30	.027	4.3285
T24-2	.945	1950	3	22.52	19.15	-	4.3281
T24-3	.946	1950	3	19.18	19.18	-	4.3286
T24-4	.927	Melted[1]		22.20	18.85	-	4.3279
T24-13	.920	1950	3	18.72	18.71		4.3297
T24-12	.861	1950	3	17.75	17.75	.011	4.3305
T24-15	.835	1950	2	17.30	17.30	.099	4.3303
T24-11	.836	1950	2	17.35	17.33	-	4.3304
T24-14	.760	1950	2	16.00	16.00	.146	4.3262
T24-20	.707	Melted[1]		15.05	15.05	.018	4.3240
T24-21	.711	1650	3	15.12	15.12	-	4.3219
T24-23	.654	1650	3	14.08	14.08	0.5	4.3185
T24-27	.614	1650	3	13.34	13.34	-	4.3141
T24-28	.556	1650	3	12.23	12.23	1.1	4.3065
T24-32	.513	1650	3	11.40	11.40	-	4.2978

Note (1)   These specimens induction zone melted in
           argon atmosphere.

T.C. = Total carbon   ⎫
                        ⎬ in wt.%
C.C. = Combined carbon ⎭

a_o = Lattice parameter in Angstrom Units

TABLE III

Comparison of Analyses for TiH_2 Starting Material and
Typical Sintered Specimen

	TiH_2 Grade E[1]	T 24-23[2]
H	3.5 - 3.8%	-
N	0.2 max	-
Na		0.001 max
Mg	0.05 max	0.001 max
Al	0.1 - 0.3	0.05 max
Si	0.1 max	0.05 max
Ca	0.05 max	
Ti	95 - 96%	High
V		.001 max
Cr		.001 max
Fe	0.1 max	.001 max
Ni		.001 max
Cu		.05 max
Zr	0.1 max	
Mo		.001 max
Sn		.001 max

(1) Metal Hydrides Analysis

(2) Jarrell Ash Analytical Lab. Report

TABLE IV

ZrC Specimens for Lattice Parameter Measurements

Spec. No.	Ratio	Temp	Time	T.C.	C.C.	a_o
Z4-1	.96	Melted[1]	-	12.05	11.2	4.6976
Z4-2	.960	Melted[1]	-	11.22	11.22	4.7010
Z4-3	.927	Melted[1]	-	10.88	10.88	4.6994
Z4-4	.831	(2)	-	13.14	9.86	4.6941
Z4-5	.693	1800	2	8.37	8.37	4.6875
Z4-6	.620	1950	3	7.54	7.54	4.6774
Z4-7	.60[3]	2200	3	-	-	4.6776
Z4-8	.583	1950	3	7.13	7.13	4.6746
Z4-9	.549	1800	2	6.74	6.74	4.6798
Z4-10	.530	1800	2	6.52	6.74	4.6726

Notes:
1. Induction zone melted in argon atmosphere
2. A commercial ZrC specimen
3. Nominal composition

T.C. = Total Wt.% Carbon

C.C. = Combined Wt.% Carbon

a_o = Lattice parameter in Angstrom Units
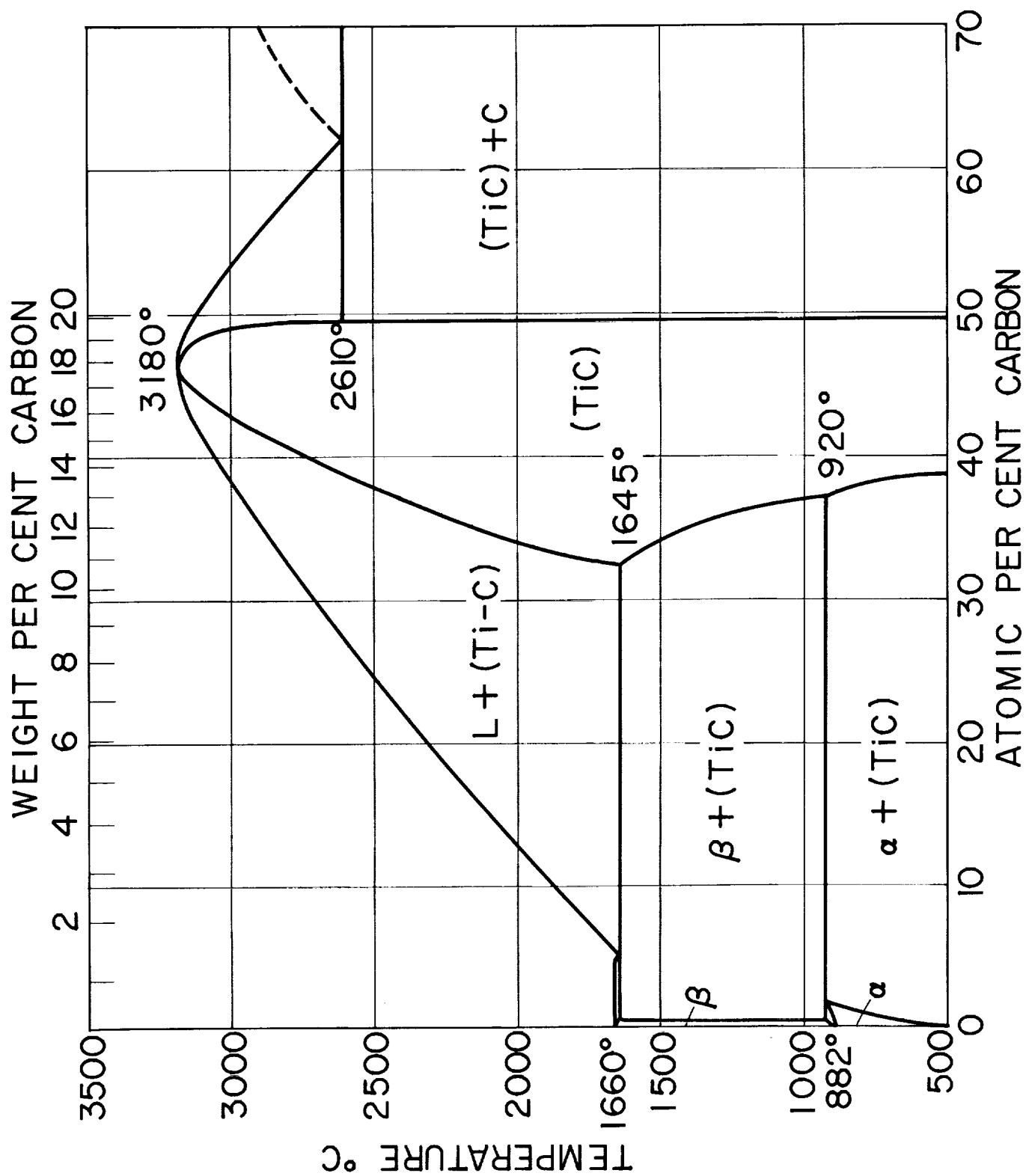
FIG. I PHASE DIAGRAM OF Ti-C SYSTEM
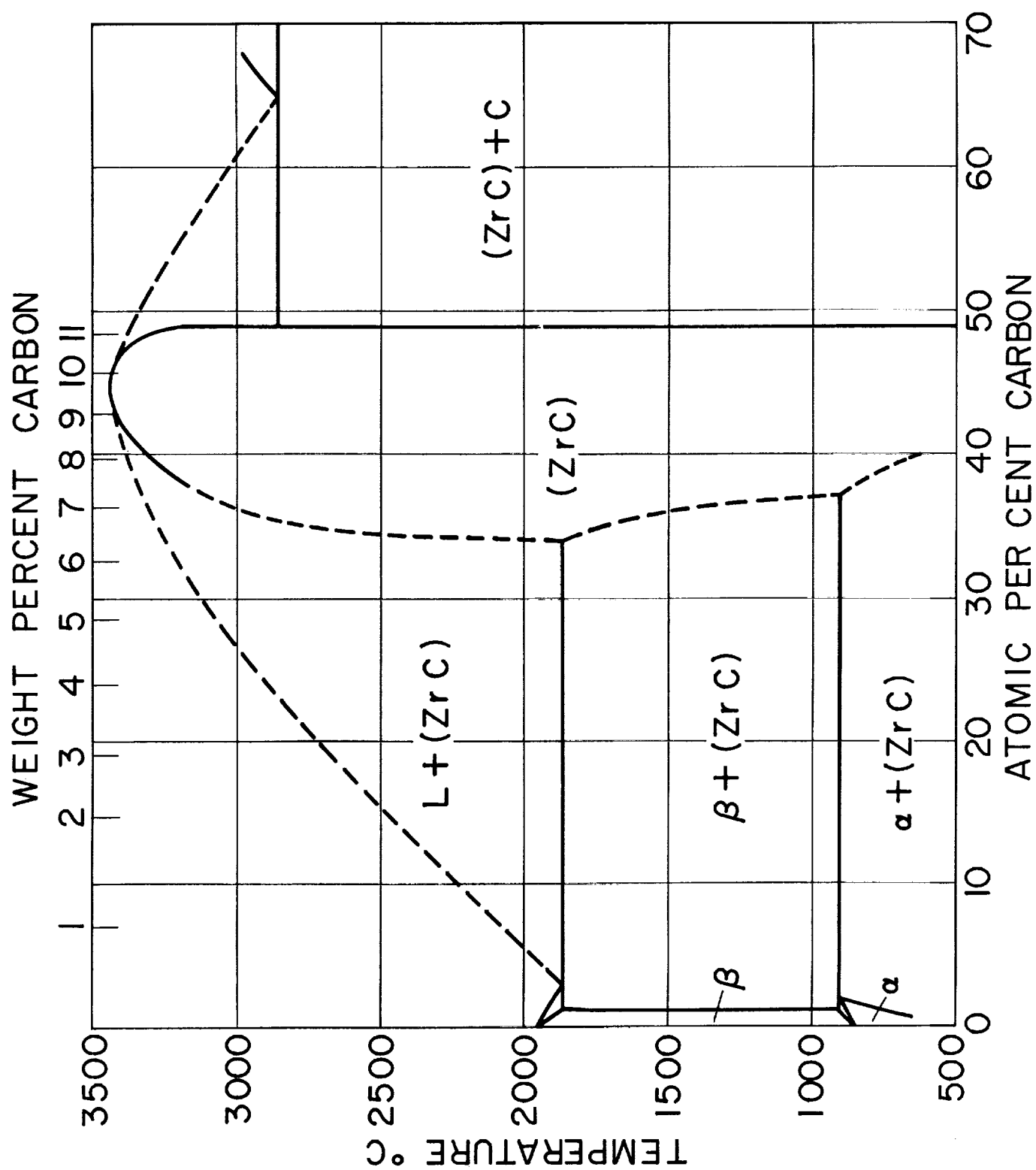
FIG. 2 PHASE DIAGRAM OF Zr-C SYSTEM

32
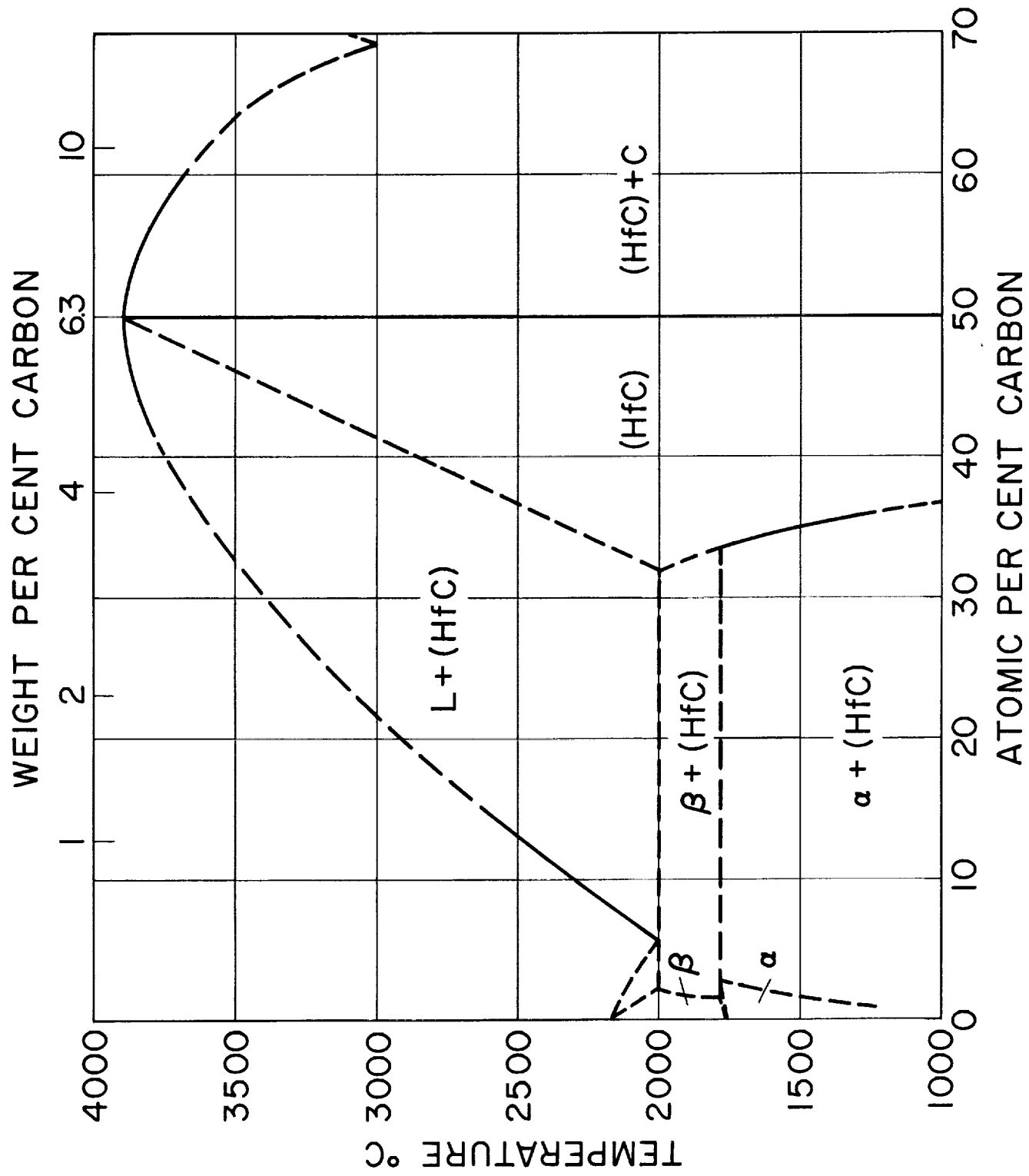
FIG. 3 PHASE DIAGRAM OF Hf-C SYSTEM

33
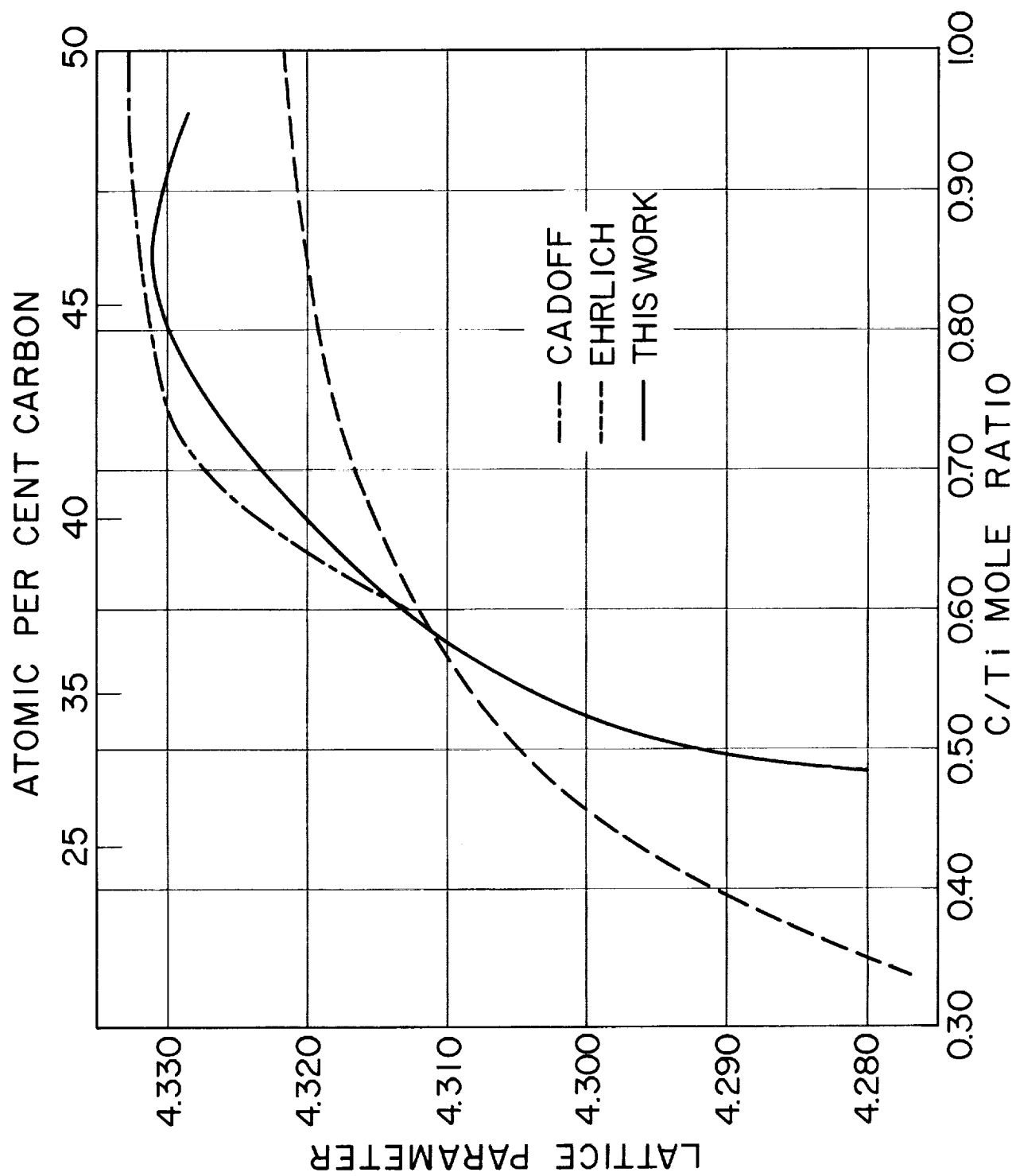
FIG. 4 LATTICE PARAMETER VS. CARBON COMPOSITION
COMPARISON OF LATTICE PARAMETER RESULTS
FOR Ti−C SYSTEM

34
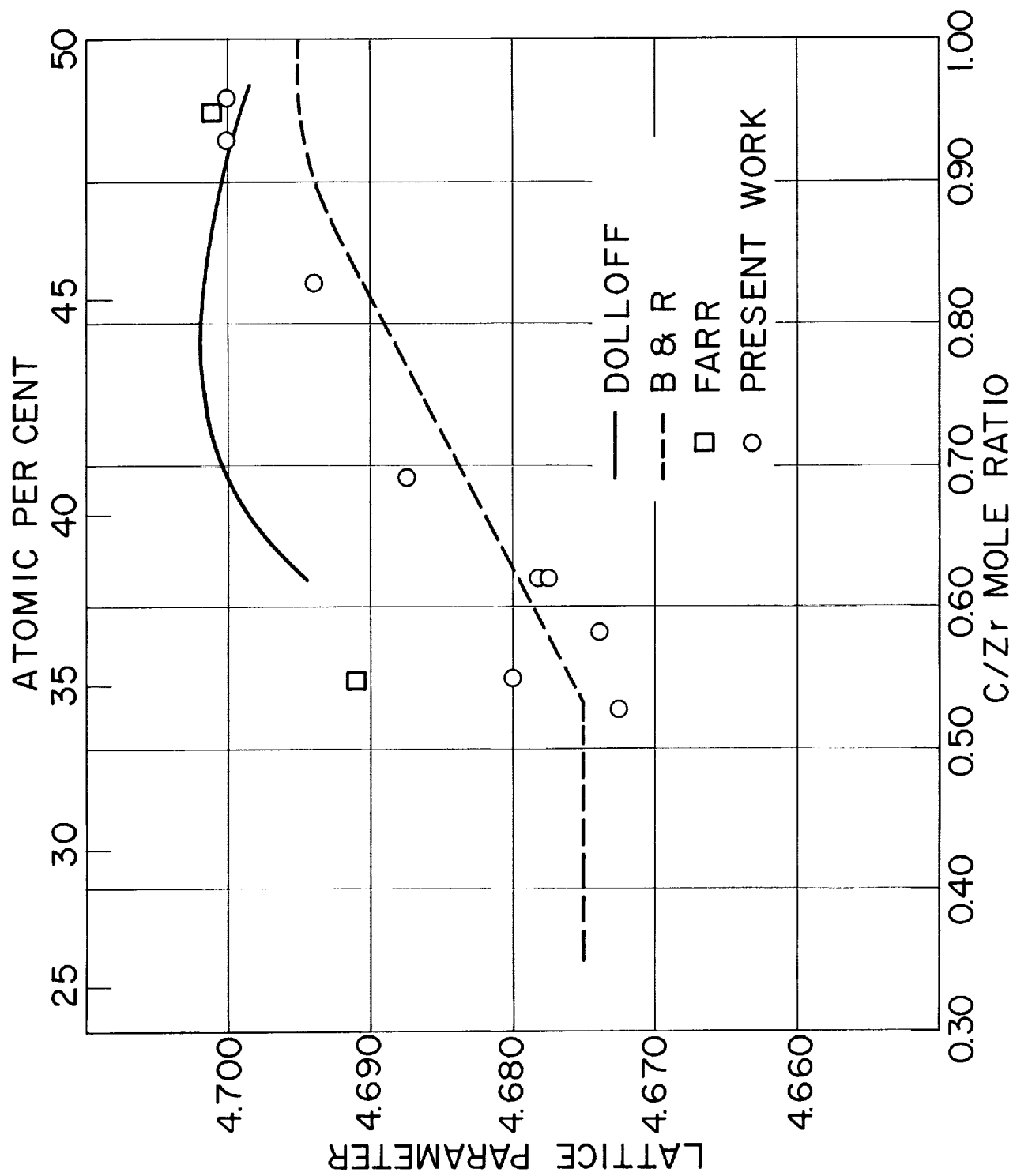
FIG. 5 LATTICE PARAMETER VS CARBON COMPOSITION
COMPARISON OF LATTICE PARAMETER RESULTS
FOR Zr-C SYSTEM

35
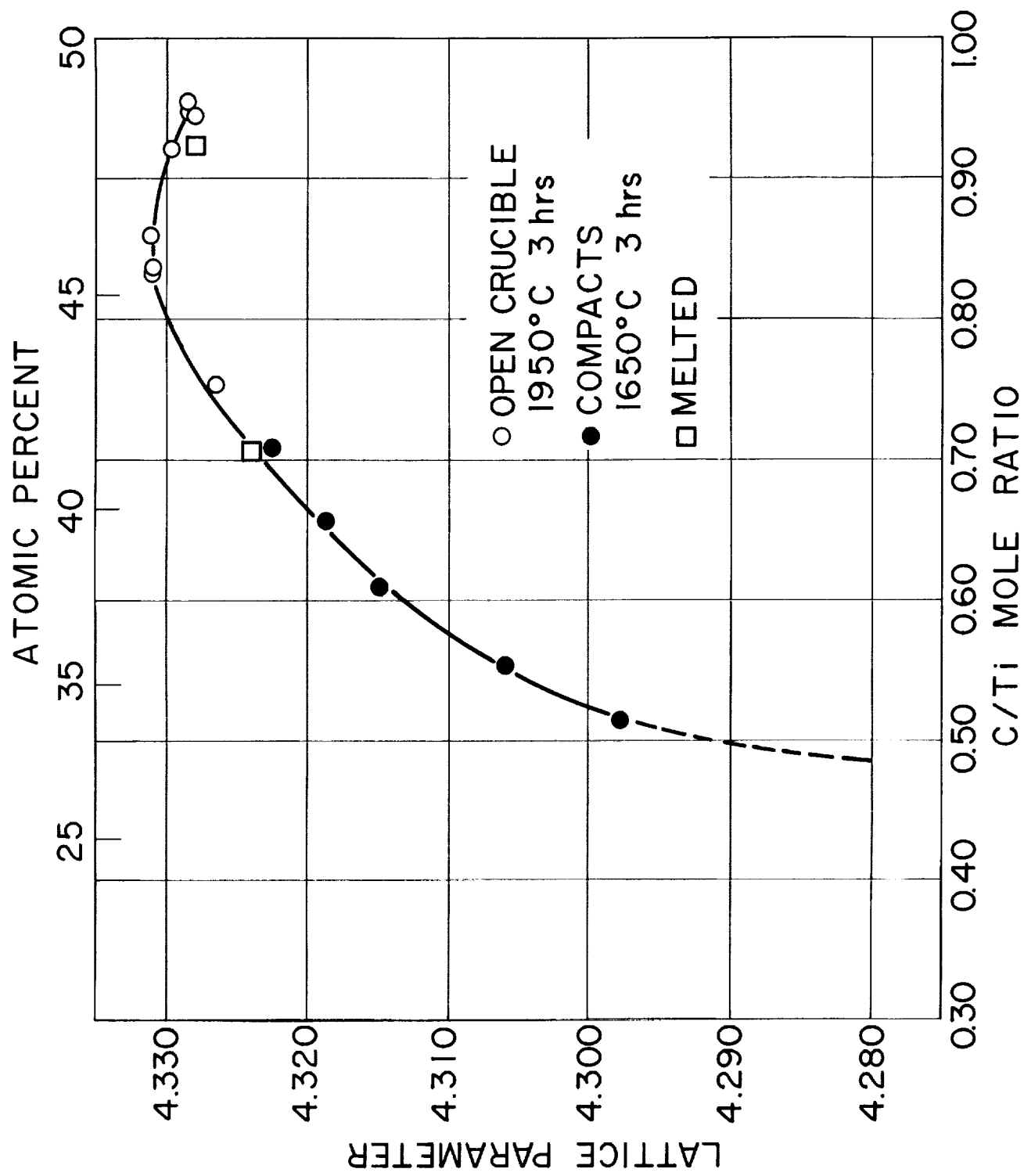
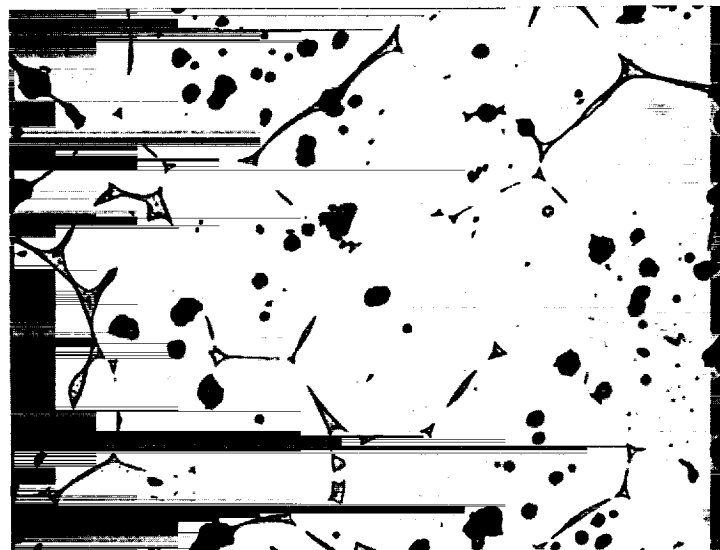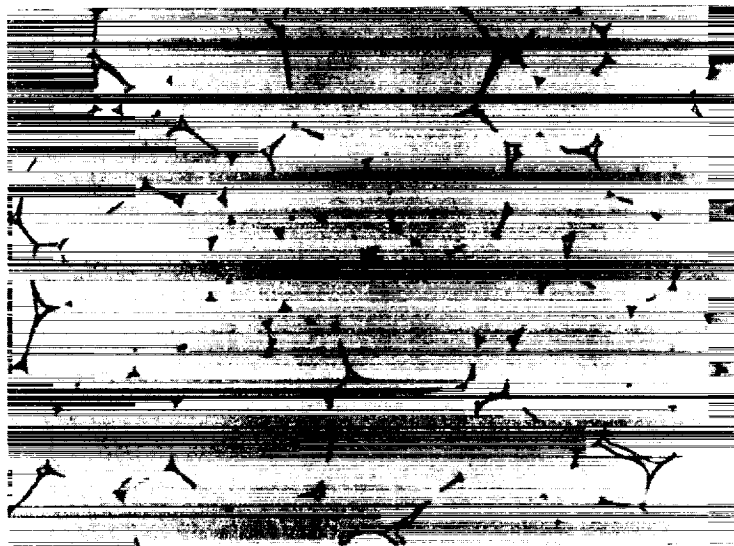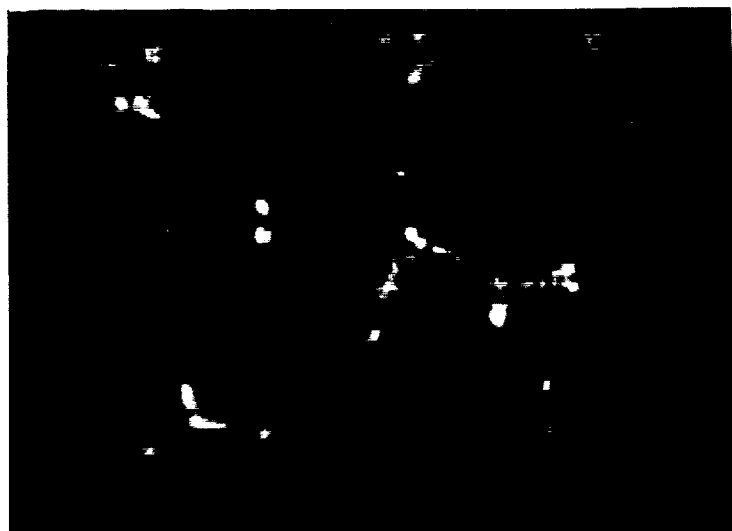FIG 6 LATTICE PARAMETER VS. CARBON COMPOSITION
TiC ALLOYS T 24 SERIES
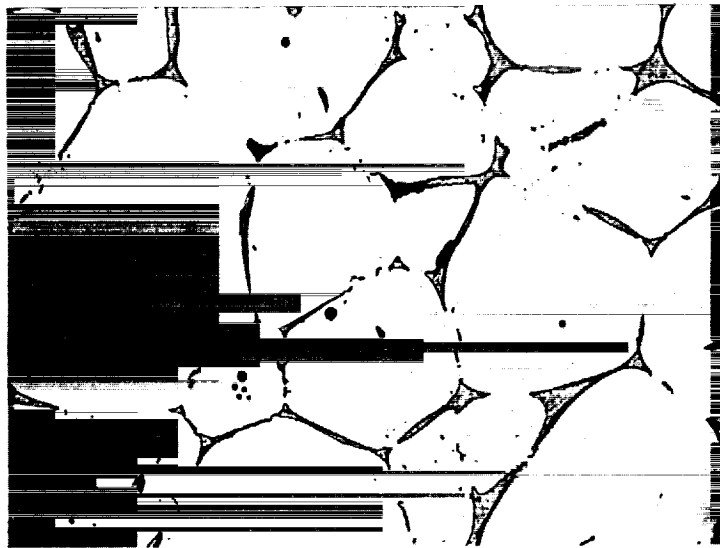
Fig. 7   TiC Sintered Specimens.   Sintered at
            1800°C 1 hr. then at 1650°C 1 hr.

                                    unetched X250

A

B

Fig. 8   TiC$_{0.63}$ Sintered Specimen With Added Iron.

A   Optical   unetched X250
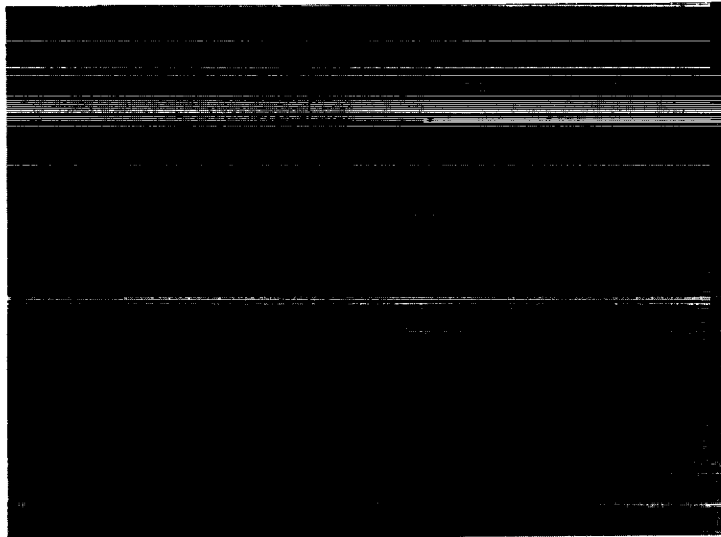B   Scanning Display of Electron Microbeam
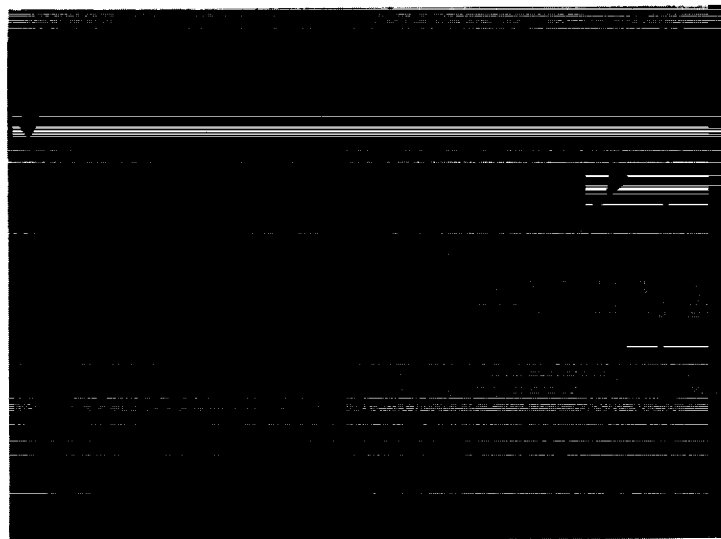   Analysis Iron K$_\alpha$ Radiation.   X420
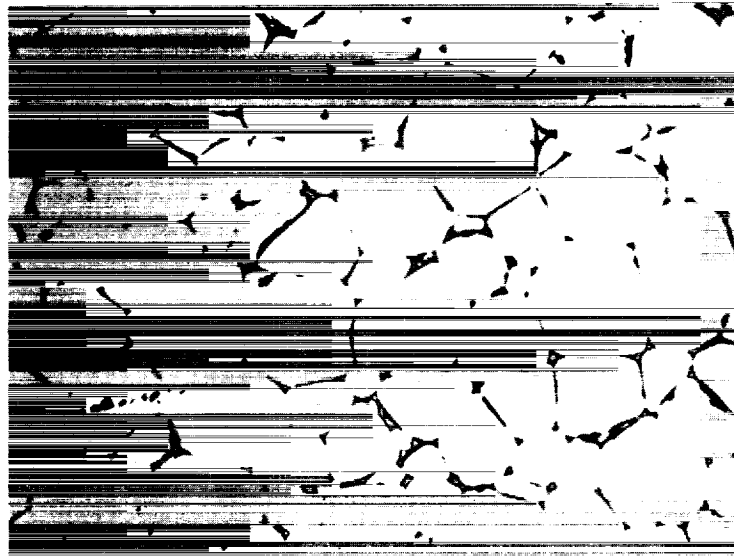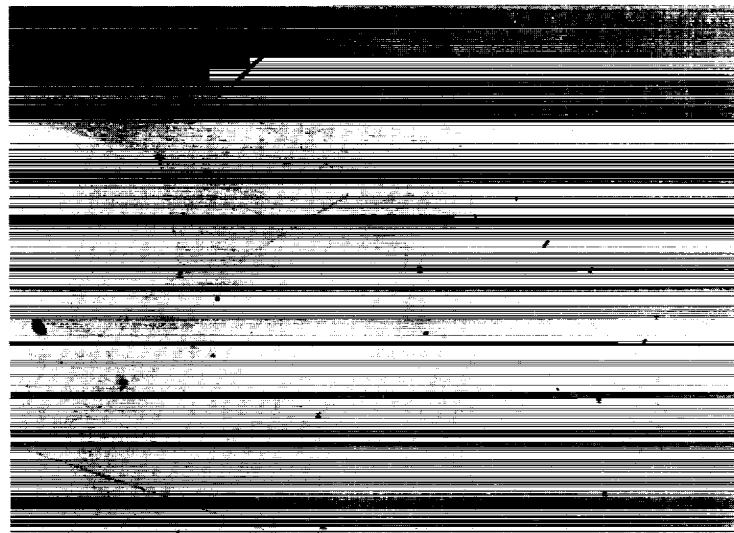
Fig. 9 TiC$_{0.85}$ Sintered Specimen With Added Iron.

A Sintered 1950°C 2 hrs. unetched X250
B Sintered 1950°C 2 hrs. then 2200°C 4 hrs.
etched X250

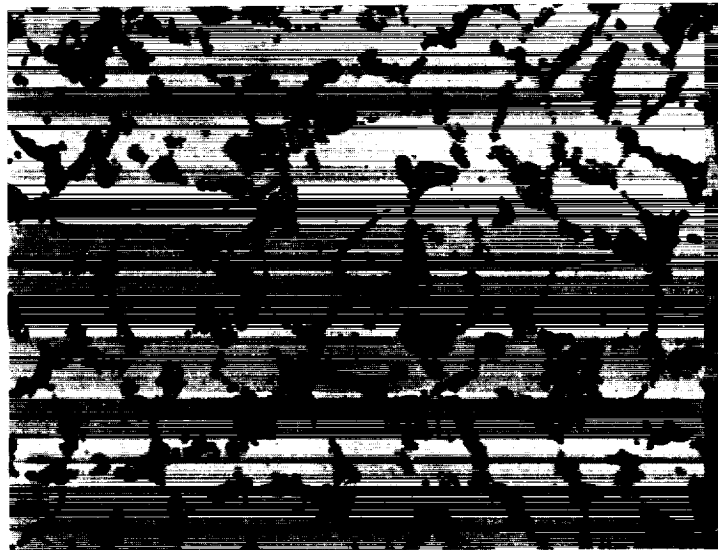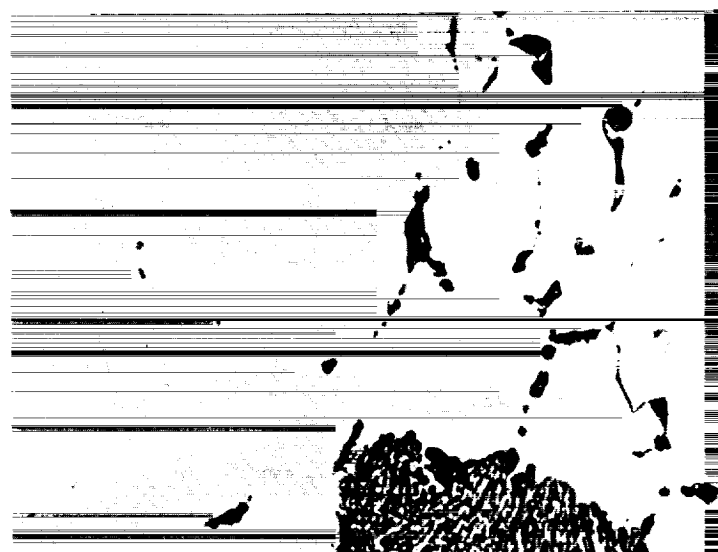Fig. 10 $TiC_{0.7}$ Induction Melted Specimen No. T24-20

    A   unetched   X250
    B   etched   X250

A

B

Fig. 11 TiC Induction Melted Specimen No. T24-4
                        unetched X250

A Area of high carbon content TiC-C eutectic
    at grain boundaries.

B Area of lower carbon content.